

Heavy metals and arsenic in the soils in the area of Narva power plants: Distribution and controlling factors

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Two world's largest oil shale-fired thermal power plants located in the North-eastern Estonia are the main sources of air pollution in Estonia. Up to 50 thousand tonnes of combustion ashes are emitted to the atmosphere annually.

Oil shale contains most of the naturally occurring chemical elements at least in trace amounts. Trace species may be realised during combustion and can pose an environmental and human risk. Soils have been considered as one of the main recipients of pollutants.

To evaluate potential hazard of contamination in the area influenced by the Narva Power Plants the geochemical mapping was carried out. Geochemical maps created basing on the ICP-MS data for major and trace elements allow illustrating spatial distribution of elements studied and outline the areas with uncommon concentrations in the soils. Well-defined areas with the highest values of elements are observed generally along the seacoast zone and to the east of the Narva region that reflect the incorporation of the Lower Ordovician shale bedrock naturally enriched in potentially toxic elements.

Mobility and availability of arsenic and heavy metals in soils was evaluated by the two-steps (milliQ water and sodium acetate) sequential extraction. The results showed that heavy metals and arsenic are leached in low quantities and attributed generally to mineral phase in the soils. The water soluble fractions are negligible (<1%). The Na-acetate extractable concentrations of Cd, Co, Cr, Pb and Zn are much higher than those obtained using water extraction. Extractability of elements depending on pH, grain size composition and soil types also as elements contribution from very various parent materials will be discussed in the presentation.

Thermodynamics of solid solutions of carbonates with non-isostructural end-members: The prediction of solubility limits with the single defect method

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Carbonates are considered as sorbents for various contaminants dissolved in aqueous solutions. Numerous studies suggested that carbonates can retain significant amounts (up to thousands of ppm) of SO_4^{2-} , SeO_4^{2-} , HAsO_3^{2-} , HPO_4^{2-} , CrO_4^{2-} , while concurrent spectroscopic and surface diffraction studies have shown that these anions, indeed, replace CO_3^{2-} units of the carbonates. The question is, can these experimental results be considered as a proof for the formation of thermodynamically stable solid solutions? Our approach to the problem is based on the assumption that the solute components obey Henry's law. This is equivalent to assuming that the enthalpy of mixing of a diluted solid solution can be approximated as a linear function of the mole fraction of the solute. The extrapolation of this line to 100% of the solute component allows defining the enthalpy of the virtual (solute) end-member, which within the same assumption forms a perfectly ideal solution with the host. We have been able to calculate the total energies of virtual end-members from the total energy of the host (carbonate) and the energies of supercells of the host with a single CO_3^{2-} unit replaced by an anion of the solute end-member. The energies were calculated from first principles. The standard enthalpies of the virtual end-members were then calculated relative to reference compounds with the same composition, whose standard thermodynamic properties are well defined. Our calculations predict vanishingly small concentrations of SO_4^{2-} , SeO_4^{2-} , HAsO_3^{2-} and HPO_4^{2-} . This suggests that carbonate 'solid solutions' formed by co-precipitation with these components are not stable in the thermodynamic sense. Experimental approaches to testing this hypothesis are discussed.